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Electrochemical NO_x Sensors for Automotive Diesel Exhaust

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ABSTRACT

New emissions regulations will increase the need for compact, inexpensive sensors for monitoring and control of automotive exhaust gas pollutants. Species of interest include hydrocarbons, carbon monoxide, and oxides of nitrogen (NO_x). The current work is directed towards the development of fast, high sensitivity electrochemical NO_x sensors for automotive diesel applications. We have investigated potentiometric NO sensors with good sensitivity and fast response when operated in 10% O₂. The sensors consist of yttria-stabilized zirconia substrates attached with NiCr₂O₄ sensing electrodes and Pt reference electrodes. A composite NiCr₂O₄:Rh sensing electrode is shown to give significantly faster response than NiCr₂O₄ alone. The exact role of the Rh in enhancing the response speed is not clear at present. However, the Rh appears to accumulate at the contacts between the NiCr₂O₄ particles and may enhance the inter-particle electronic conduction. Ongoing testing of these sensors is being performed to elucidate the sensing mechanisms and to quantify cross sensitivity to, for example, NO₂.

INTRODUCTION

Increasingly stringent emissions regulations will introduce a need for compact, inexpensive sensors for monitoring and control of regulated exhaust gas pollutants including hydrocarbons, carbon monoxide, and oxides of nitrogen (NO_x). Significant progress has been made towards the development of electrochemical sensors using ionically conducting ceramic electrolytes, usually yttria-stabilized zirconia (YSZ), and catalytically active metal oxide sensing electrodes [1, 2, 3]. The suitability of numerous single- and mixed-metal oxides for use as NO_x sensor electrodes, usually in air, has been explored in the literature [4, 5]. Despite the prior investigations, however, reliable, cost effective sensors suitable for diesel exhaust gas applications have not yet emerged. Improvements are still needed in sensitivity, response time, reliability, and cross-sensitivity.

The current work is directed towards the development of fast, high sensitivity electrochemical NO_x sensors for automotive diesel exhaust monitoring. The high oxygen content (5-15%) of the diesel exhaust suggests the use of a potentiometric sensor using the mixed potential response of catalytic metal oxide electrodes on a solid ionic conducting electrolyte. This mixed potential response occurs as a result of the multiple, competing oxidation/reduction reactions which can occur in the presence of a composite gas containing multiple species such as O₂, NO, NO₂, etc.. To facilitate sensor development, this work was performed by applying catalytic electrodes to a standard O₂ sensor substrate. Mixed potential response to NO in 5-15% O₂ was monitored as a function of gas temperature and sensor substrate temperature.

EXPERIMENTAL DETAILS

The NO sensors were fabricated by modification of multi-layer O₂ sensors. The O₂ sensors have Pt sensing and reference electrodes on a yttria-stabilized zirconia (YSZ) substrate, and are laminated together with an integrated resistive heater. To enhance the NO sensitivity, the sensors were modified by coating ~2 μm of sub-micron NiCr₂O₄ powder over the Pt sensing electrode using a colloidal spray deposition technique, and sintered at 900 °C for 1 hr. Composite NiCr₂O₄:Rh layers were formed by a proprietary technique which involves infiltration of small amounts of Rh into the sintered NiCr₂O₄ electrode. In all cases, the NiCr₂O₄ or composite coatings extended past the edges of the underlying Pt electrode to make direct contact with the YSZ electrolyte. The sensors are heated by applying a current to the resistive heater, and the temperature determined from the heater resistance. The heater was calibrated using independent measurements of heater resistance versus furnace temperature in the range from room temperature to 650 °C. The O₂ sensors were intended to operate with the reference electrode isolated from the test gas (i.e. air reference), however in this study both sensing and reference electrodes were exposed to the test gas stream for the NO testing. The sensor and experimental setup are shown schematically in Figure 1.

NO sensing experiments were performed in a quartz tube (inside diameter = 1.75 cm) inside a tube furnace. Pt wires were used to connect the external leads to the sensor electrodes. Unless otherwise specified, all tests were performed using 500 ppm NO in 10% O₂, balance N₂,

at a flow rate of 1000 ml/min. The face velocity of the gas flowing through the reaction tube at this flow rate is ~7 cm/s, which is significantly less than in automotive exhaust. A standard gas handling system was used to deliver the gasses to the reaction tube. The configuration of a typical sensor and the testing configuration are shown in Figure 1. An electrochemical interface was used to measure open circuit potentials at 0.5 s intervals. Tests were performed with gas temperatures ranging from 250-350 °C, and sensor temperatures from 400-600 °C.

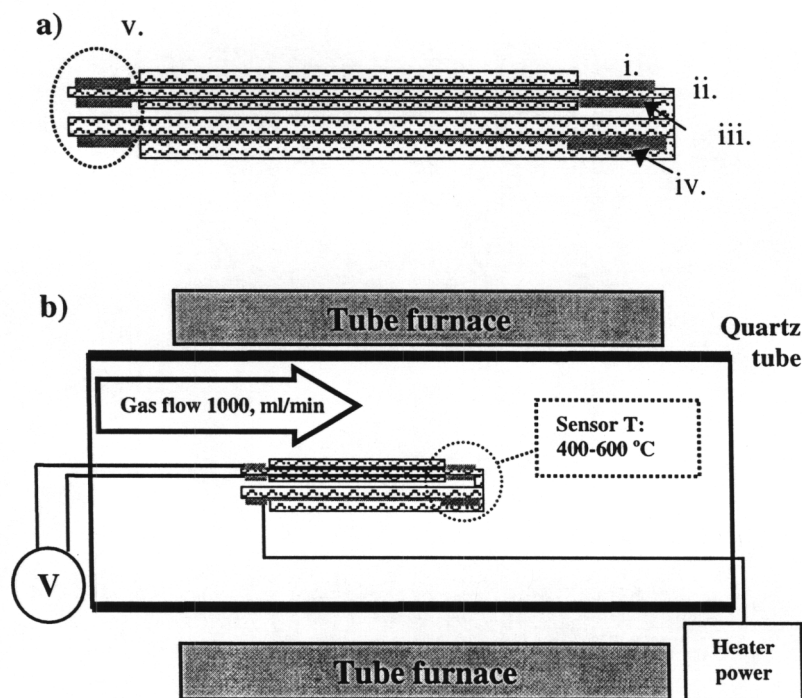


Figure 1: a) Schematic of the NO sensor showing i. sensing electrode, ii. YSZ electrolyte, iii. reference electrode, iv. resistive heater, and v. pads for making connections to the electrodes and heater. b) The sensor testing setup.

RESULTS

The NO sensors were tested in flowing gas, 10% O₂, and the response to the addition of 500 ppm NO was monitored. Figure 2 shows typical results for sensors with NiCr₂O₄ and composite (NiCr₂O₄:Rh) electrodes, with a gas temperature of 250 °C and sensor temperature of 450 °C. The data show the sensors to have a baseline, i.e. 10% O₂ without NO, of approximately -3 mV. With the addition of 500 ppm NO to the gas stream, the sensor responds with a significant negative potential at the sensing electrode (relative to the reference electrode). It is generally assumed that the NO electrochemically combines with O²⁻ ions from the YSZ at the YSZ/electrode interface. In the presence of oxygen, this reaction combines with the electrochemical reaction for oxygen (with the YSZ) to form a local cell, with a net reduction in the overall potential. This response is described as a mixed potential response, and occurs as a result of the simultaneous, competing oxidation/reduction reactions at the electrode. The generally accepted form of these reactions is given as [6]



While generally accepted, this description of the sensing mechanism is probably oversimplified. There is experimental evidence that the response is not entirely determined by the properties of the gas/electrode/YSZ interface, but is also affected by the electrode thickness and microstructure, and by the nature of the electrical connection to the electrode [7]. It should also be noted that under the present experimental conditions, the measured response is not strictly equivalent to the mixed potential at the sensing electrode, but rather to the difference between the mixed potentials at the sensing and reference electrodes. Ideally, these electrodes are selected so that the reference electrode is very much less sensitive to the test species, NO, than the sensing electrode. Alternatively, the reference electrode can be removed from the test gas stream and

exposed to a constant atmosphere (air).

In Figure 2, both sensors exhibit responses that approach, or exceed -25 mV from the baseline, however it is immediately apparent that the composite electrode responds significantly faster than the NiCr₂O₄. This is particularly evident in the time required to achieve a stable response, which takes many minutes for the NiCr₂O₄ sensor. Equally important, however, is

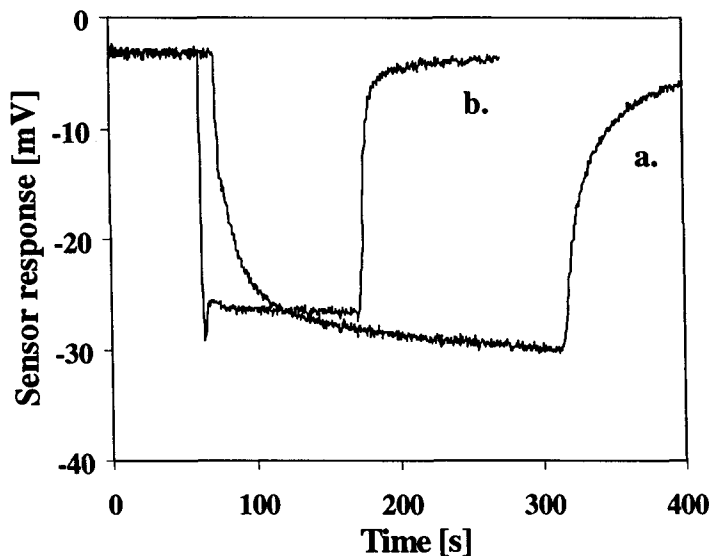


Figure 2: Response to 500 ppm NO in 10% O₂ for sensors with a. NiCr₂O₄ and b. composite sensing electrodes. Gas: 250 °C, sensor: 450 °C.

the recovery time when the NO is removed from the gas stream. Minimizing this time is crucial to the development of a deployable NO sensor suitable for exhaust monitoring and control. Because the sensor with the composite electrode recovers the baseline so much faster than the NiCr_2O_4 sensor, further testing was performed to evaluate the relative sensitivity and speed of these sensors.

Figure 3 shows the response to 500 ppm NO in 10% O_2 for each of the two sensors as a function of sensor temperature for different gas temperatures. The results show that at intermediate sensor temperatures, 425–500 °C, the sensor with the composite electrode has a sensitivity which is comparable to the NiCr_2O_4 sensor. At sensor temperatures below ~450 °C, the NiCr_2O_4 sensor had larger responses, however it was difficult to acquire reliable data due to the very long equilibration times required. Conversely, above 500–550 °C the composite sensor had essentially no response. This seems to indicate multiple, competing mechanisms in the sensing process. It is well known that Rh is highly catalytic to certain active gas species, however the quantity of Rh added to form the composite electrode is very small. In fact, during SEM analysis of the electrode microstructure it is very difficult to distinguish between the electrodes with and without the Rh. In other words, in the composite electrode nearly all the surface area of the (porous) electrode appears to be made up of the NiCr_2O_4 particles. Thus, it is unlikely that the added Rh dominates the catalytic properties, but rather seems to promote the speed of the NiCr_2O_4 response. Very careful inspection using SEM and EDX indicates the presence of thin Rh necks forming between some of the NiCr_2O_4 particles. It is presumed that these metallic interparticle contacts promote the charge transfer through the electrode and thereby quicken the response. This proposed mechanism is, at the present time, speculative and deserves further investigation since it has potential implications to a broad range of sensor development applications.

In all cases, the composite sensor had significantly faster response times than the NiCr_2O_4 sensor. For the purpose of tabulating this effect, we have defined the “response speed” as the time, after removing 500 ppm NO from the gas stream, for the sensor to recover the middle 1/3 of the potential difference between its full response and its baseline (i.e. the time during

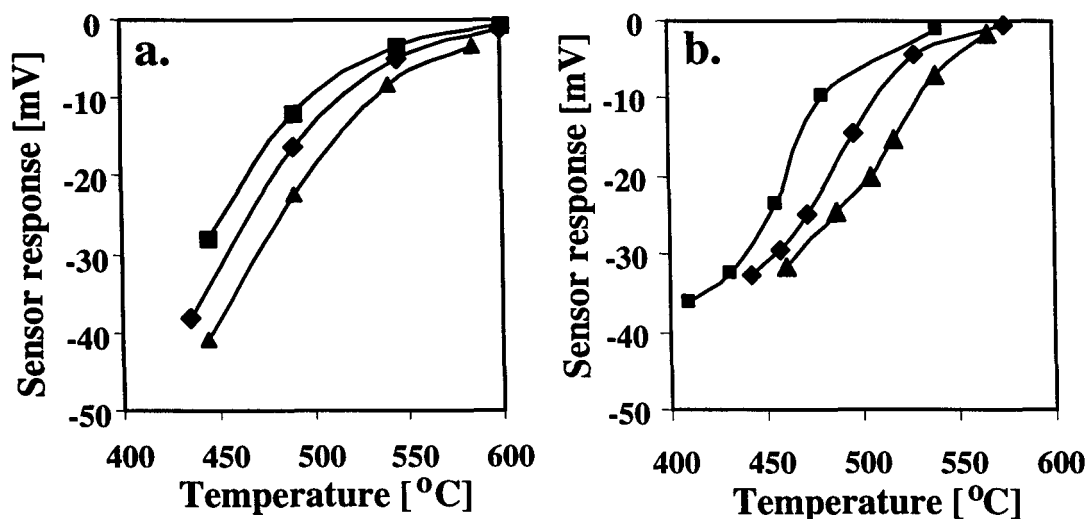


Figure 3: Sensor response to 500 ppm NO, 10% O_2 , as a function of sensor temperature for sensors with a) NiCr_2O_4 and b) composite electrodes. Gas temperature: —■— 250 °C, —◆— 300 °C, —▲— 350 °C.

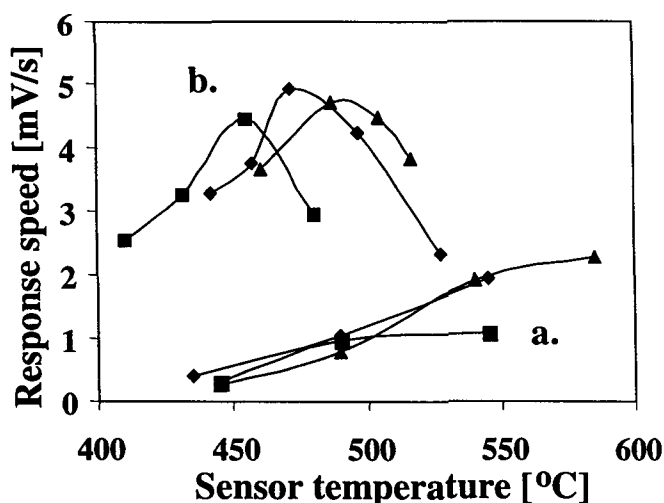


Figure 4: Response speed (30-70% recovery from 500 ppm NO) as a function of sensor temperature for sensors with a) NiCr₂O₄ and b) composite electrodes. Gas temperature: —■— 250 °C, —◆— 300 °C, —▲— 350 °C.

recovery from 70% of the full response to 30% of the full response). These data are shown for the two sensors in Figure 4, again as a function of sensor temperature. The data indicate that under all conditions the composite sensor is significantly faster than the NiCr₂O₄ sensor. The speed of the NiCr₂O₄ sensor is not sensitive to gas temperature over the range tested, however the composite sensor exhibits a high-temperature roll-off in response speed which is sensitive to the gas temperature. The reason for this high-temperature roll-off is not clear at present.

Additional measurements were performed to evaluate the sensitivity to the composite sensor to varying levels of O₂, NO and NO₂. The response to different NO concentrations in 10% O₂ (gas temperature 250 °C, sensor temperature 450 °C) is shown in Figure 5. The response is approximately logarithmic with the NO concentration from 100-500 ppm, but deviates somewhat at concentrations below ~100 ppm. This may be due to the competing effects of the catalytic activity of the Pt counter electrode, which was also exposed to the test gas in this configuration, or may be due to a systematic error in the NO concentration measurement (equivalent to ~25 ppm). Under these operating conditions, it was determined that over the range of 5-15% O₂, the sensor baseline shifted approximately +2 mV, or <10% of the response to 500 ppm NO. Over that same range of O₂ concentration, the response to 250 ppm NO, as measured from the respective baselines, was constant. Finally, it was noted that the sensitivity to NO₂ was comparable to, or slightly larger than the NO sensitivity, and opposite in sign as expected from the oxidation/reduction behavior of NO₂ relative to NO.

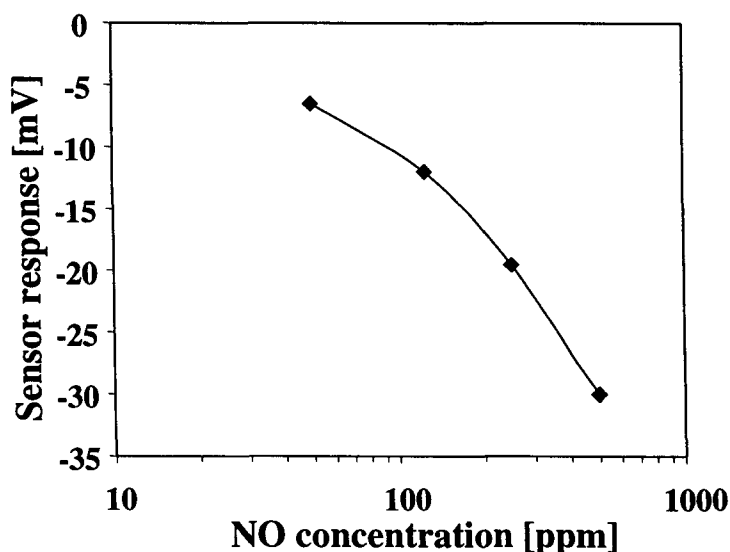


Figure 5: NO response as a function of NO concentration (in 10% O₂) for the composite-electrode sensor. Gas temperature: 250 °C, sensor temperature 450 °C.

CONCLUSIONS

We have investigated potentiometric NO sensors with good sensitivity and fast response when operated in 5-15% O₂. The sensors consist of yttria-stabilized zirconia substrates attached with NiCr₂O₄ sensing electrodes and Pt reference electrodes. While sensors with a NiCr₂O₄ sensing electrode exhibit a significant NO response under the test conditions, response times are too long to be of use for automotive exhaust monitoring and control. A composite NiCr₂O₄:Rh sensing electrode is shown to give significantly faster response than NiCr₂O₄ alone. It is postulated that the Rh, which appears to accumulate at the contacts between the NiCr₂O₄ particles, may enhance the inter-particle electronic conduction and thus speed the sensor response. Ongoing testing of these sensors is being performed to elucidate the sensing mechanisms and to quantify cross sensitivity to, for example, NO₂.

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